

**Influence of the microstructure on the nucleation and growth of chromate conversion coatings on Al alloys**

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Aluminum alloys for aircraft applications are commonly treated with a chromate conversion coating (CCC) to improve the corrosion resistance. However the development of chromium-free treatments is becoming a top priority since the production, storage and use of chromate baths lead to several environmental and health related problems. A better understanding of the mechanisms of nucleation, growth and corrosion protection of the CCC is necessary to find out how the excellent properties of the CCCs can be obtained using compounds with lower impact on environment and health.

Many authors have pointed out the strong effect of the intermetallic particles on the formation of the CCCs and as consequence on their corrosion properties [1-4]. However, the exact role played by the particles on the nucleation and growth mechanisms of CCCs is not yet completely clear. Recently, *McGovern et al.* [5] have shown by means of Raman spectroscopy that the chromate film formed on Cu-rich particles in AA2024 is much thinner than on the matrix, in agreement with the results reported by *Juffs et al.* [6]. However, the former claimed that the formation of CCC on the intermetallics is hindered due to adsorption and degradation of ferricyanide compounds at copper-rich regions, whereas the latter stated that it is due to the presence of a thick aluminum oxide film at these locations. Furthermore, *Kendig et al.* [3] in accordance with our own results [7] have shown that the nucleation of the chromate film starts on the intermetallics.

This apparent contradiction between the investigations carried out by different researchers is believed to result from the use of both different times of immersion in the chromate solution and different surface preparation routes. In the present work, both the early stage of the nucleation and the subsequent growth of CCC on AA2024-T3 and AA7075-T6 were studied by means of SEM, EDS, and AFM techniques. Coupons of these two aluminum alloys were immersed in a commercial chromate bath (Alodine 1200) after different surface preparation procedures: (a) polishing, (b) acid pickling in H<sub>2</sub>SO<sub>4</sub>/H<sub>3</sub>PO<sub>4</sub> on both polished and as-received surface, (c) treatment *b* followed by dipping in HNO<sub>3</sub>/HF solution. The duration of the immersion in the Alodine bath was varied from very short times (3, 15, 30 seconds) to more conventional times (60, 180 seconds) enabling to distinguish the effect of the intermetallics on the nucleation and on the growth mechanisms of CCC.

It was found that the formation of CCC started at the Cu-containing intermetallics (figures 1 and 2), which act as cathodic sites (figure 3) and then favor the reduction reaction of Cr(VI) to Cr(III). This led to the formation of a thin and dense chromate film on top of the intermetallics that renders them less active, since it hinders the electron transfer at these locations causing a slowing down of the film deposition. Therefore, in the case of the polished samples the further growth of the CCC took place mainly on the matrix resulting in the formation of a thicker layer in comparison with that deposited on the intermetallics during the first few

seconds of immersion in the Alodine bath. However, when the samples were immersed only in the H<sub>2</sub>SO<sub>4</sub>/H<sub>3</sub>PO<sub>4</sub> solution the matrix became strongly enriched in copper and the deposition of the CCC was hindered, whereas the immersion in the HNO<sub>3</sub>/HF solution resulted in the almost complete removal of both the copper enrichment and the intermetallics enabling the formation of a very homogeneous CCC.

Based on these results it can be concluded that the availability of cathodic intermetallics on the aluminum surface leads to a heterogeneous nucleation of the CCC, which are sites of defects in the layer. Therefore, a proper surface preparation is a necessary condition to obtain a well protective chromate film.

**References**

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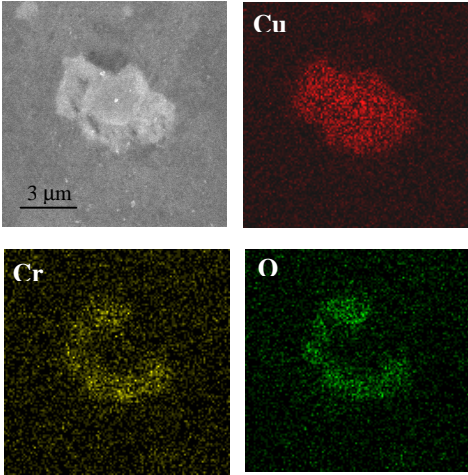


Fig. 1: SEM micrograph and EDS maps of AA2024-T3 surface after 3 seconds of immersion in the Alodine bath.

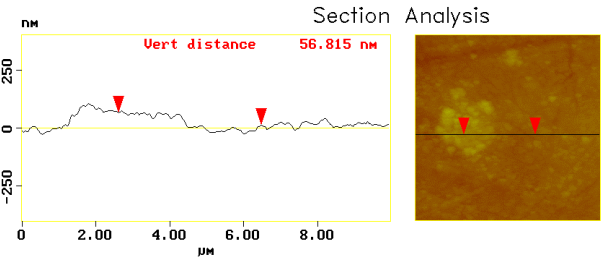


Fig. 2: AFM topographic map of AA2024-T3 (10μmx10μm) after 3 seconds of immersion in the Alodine bath.

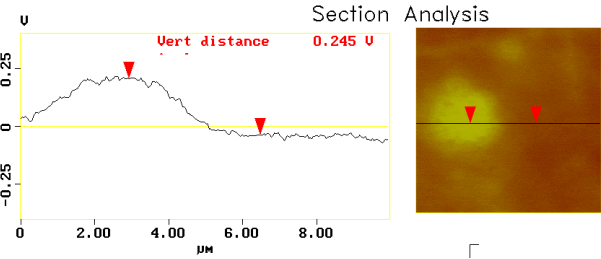


Fig. 3: AFM potential map of AA2024-T3 (10μmx10μm) after 3 seconds of immersion in the Alodine bath.